

Resonant Inelastic Soft X-Ray Scattering of CuGeO_3 and CuO

T. Schmitt, L.-C. Duda, J.-H. Guo, and J. Nordgren

Department of Physics, Uppsala University, Ångström Laboratory, Box 530, S-75121 Uppsala, Sweden

INTRODUCTION

The insulating cuprates build an interesting subgroup of the 3d transition metal compound family because of their extraordinary low-temperature behavior. Several cuprate compounds display phase transitions to superconducting electronic states. We investigated CuGeO_3 which possesses an unusual Spin-Peierls state below $T_{\text{SP}} = 14$ K and is an orthorhombic antiferromagnetic insulator at room temperature [1]. In order to understand the underlying mechanism of the Spin-Peierls transition it is essential to understand the electronic structure of this material. In particular the study of the valence band of the Cu-O octahedra is supposed to reveal valuable experimental knowledge. Therefore, it is reasonable to investigate the variation of the electronic properties compared with the simple cupric oxide CuO .

In the present work high-resolution resonant inelastic soft x-ray scattering (RISXS) at Cu 3s- and O 1s-resonances of CuGeO_3 and CuO were performed. Soft x-ray absorption spectroscopy (SXAS) was employed to determine the resonant excitation energies. RISXS can be interpreted as an energy-loss in resonantly excited soft x-ray emission spectra (SXES). Since RISXS is not core-hole lifetime resolution limited, it is capable to resolve subtle features in the electronic structure reflecting low-energy local electronic excitations [2].

EXPERIMENTAL

The investigated CuGeO_3 ($15 \times 5 \times 0.1 \text{ mm}^3$ in size) and CuO ($4 \times 1.5 \times 1.5 \text{ mm}^3$ in size) samples were single crystals. All experiments were performed at the undulator beam line 7.0.1 with a spherical-grating monochromator at the Advanced Light Source (ALS), Lawrence Berkeley Laboratory. The SXAS spectra were measured by recording the total electron yield (TEY) and the fluorescence yield (FY) while scanning the photon energy of the incident monochromatized synchrotron radiation. The monochromator energy band pass used for all SXAS spectra and for the resonantly excited SXES spectra was approximately 0.15 eV. TEY absorption spectra were recorded by measuring sample current and FY absorption spectra were measured with a channel electron multiplier. The SXAS spectra were normalized to the photo current from a clean gold mesh introduced into the synchrotron radiation beam in order to correct for intensity variations of the incident x-ray beam. The soft x-ray emission spectra (SXES) were recorded with a high-resolution Rowland-mount grazing-incidence grating spectrometer [3] with a two-dimensional detector at a resolution of about 0.15 eV.

RESULTS AND DISCUSSION

The inset in Fig. 1 displays the Cu 3s SXAS spectrum of CuGeO_3 recorded in FY mode. High-resolution resonant SXES spectra were taken at the Cu 3s-resonance at the energies marked by arrows in the absorption spectrum. The SXES spectra in Fig. 1 are plotted against an energy loss scale relative to the excitation energies to show RISXS features. These scattering spectra show distinct photon energy loss structures in the region of 1-2 eV below the elastic peak.

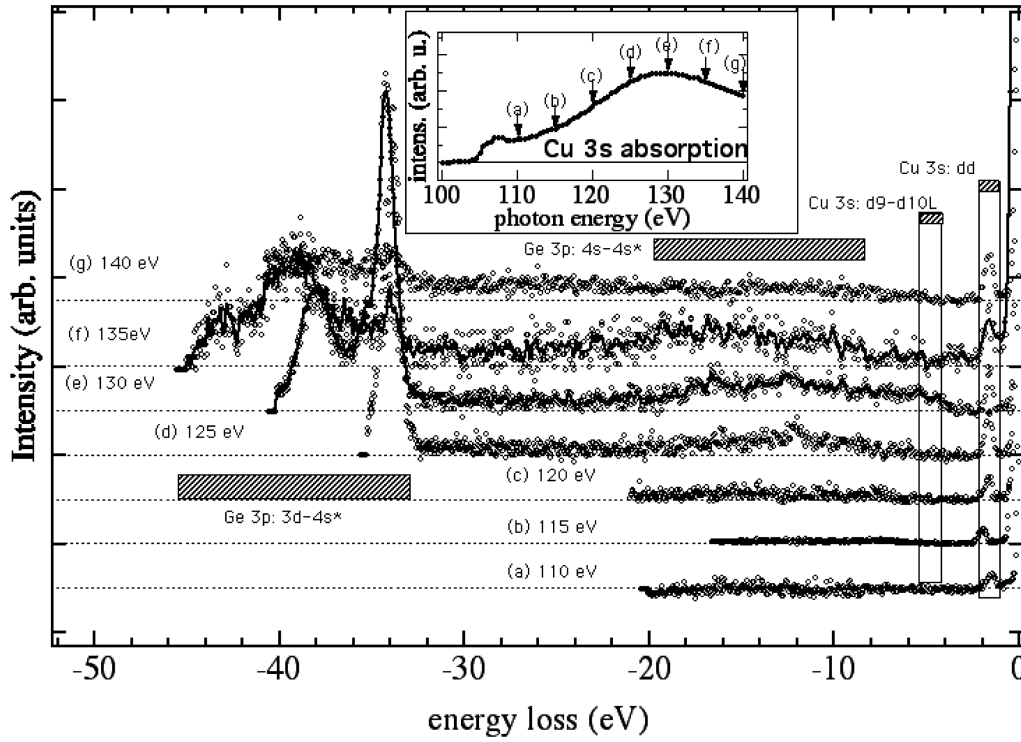


Figure 1. Resonant inelastic soft x-ray scattering spectra and Cu 3s absorption spectrum (inset) of CuGeO_3 . The excitation energies are marked by arrows in the absorption spectrum (inset).

We attribute these to dd-excitations arising at the 3s-resonance (at about 120 eV) indirectly after a Cu 3s - 4p transition. Remarkably, the resonance enhancement is detected over an at least 30 eV wide energy range. The band starting at about -6 eV could be due to charge transfer transitions involving oxygen ligand bands, i.e. $\text{Cu } 3d^9 - 3d^{10}\underline{L}$. Two other structures detected in the RISXS spectrum were found to arise through Ge 3p-resonance excitation (at 125 eV excitation energy, i.e. very close to the Cu 3s-resonance). The first one (-12 eV to -18 eV) is Ge 3p - 4s RISXS (Ge $4s \rightarrow 4s$ transition) and the second one (-33 eV to -39 eV) is Ge 3p - 3d RISXS (Ge $3d \rightarrow 4s$ transition). The spectral intensities of these scattering structures are very strong and present a high-resolution map of the unoccupied Ge 4s-band. By coincidence the Cu 3s and Ge 3p binding energies are very close and this raises the question whether these states are strongly hybridized. However, the relatively large atomic distance between Ge and Cu sites and the effective screening by the O octahedra make this hard to imagine. We argue that the inelastic scattering at Cu 3s-resonances yields in principal the same kind of information as at the Cu 1s-resonances but with much better signal-to-noise ratio and the possibility to achieve very high resolution.

Moreover, RISXS at O 1s-resonance of CuO (see Fig. 2) and CuGeO_3 [4] (not shown here) have been studied. We argue that while the RISXS O1s structure for CuGeO_3 most likely originates from a dd-excitation, the loss energies in the case of CuO are too high to come from the same kind of excitation. Instead, this must be evidence of Zhang-Rice-Singlet [5] formation (loss feature around 529 eV in Fig. 2). This also seems to be corroborated by model calculations [6] using the Anderson Impurity approach.

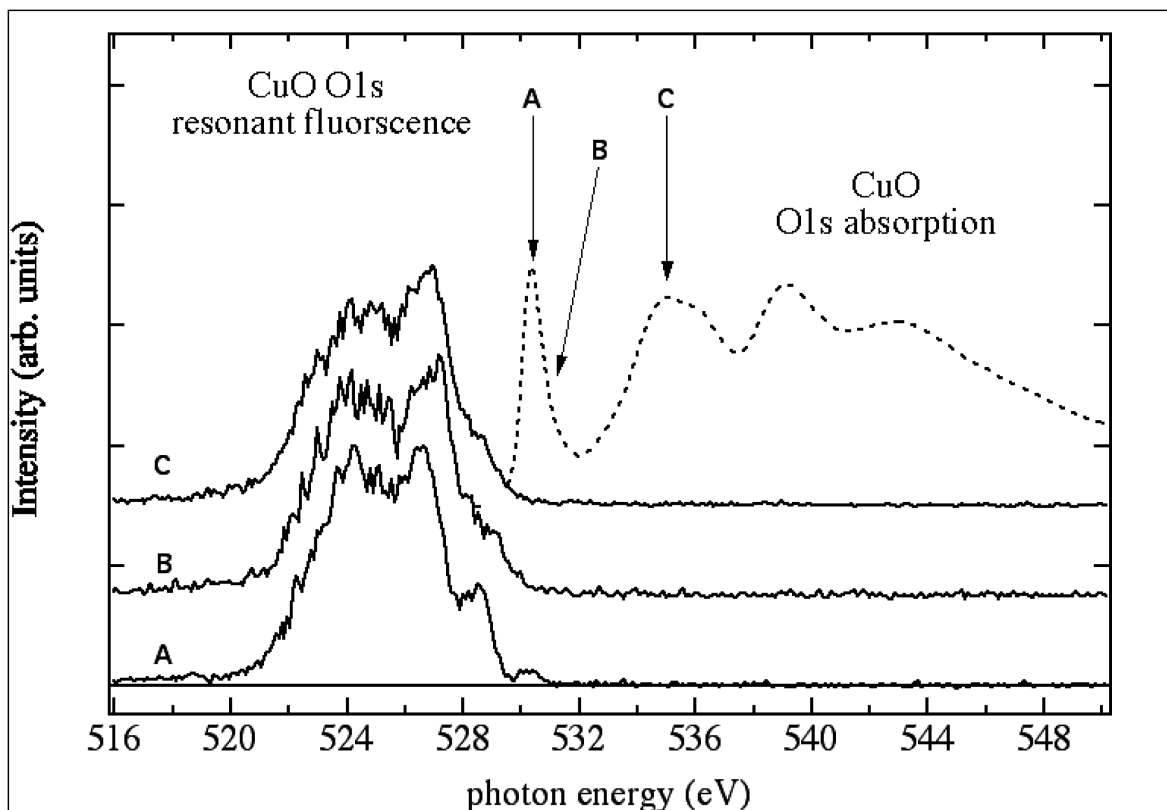


Figure 2. Resonant soft x-ray emission spectra (full lines) and O 1s absorption spectrum (dashed line) of CuO. The resonant excitation energies (A, B and C) are marked by arrows in the absorption spectrum.

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REFERENCES

1. J. P. Pouget, et al., Phys. Rev. Lett. **72**, 4037 (1994).
2. P. Kuiper, et al., Phys. Rev. Lett. **80**, 5204 (1998).
3. J. Nordgren, et al., Rev. Sci. Instrum. **66**, 1690 (1989).
4. L.-C. Duda, et al., Phys. Rev. B **61**, 4186 (2000).
5. F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, R3759 (1988).
6. K. Okada and A. Kotani, Phys. Rev. B **63**, 045103 (2001).

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Principal investigator: Laurent-C. Duda, Department of Physics, Uppsala University, Ångström Laboratory, Box 530, S-75121 Uppsala, Sweden. Email: Laurent.Duda@fysik.uu.se. Telephone: +46-(0)18-471-3512.